

**PROCESS FOR MONITORING THE GASEOUS
ENVIRONMENT OF A CRYSTAL PULLER
FOR SEMICONDUCTOR GROWTH**

5 CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority from U.S. Provisional Application Serial No. 60/257,646, filed on December 22, 2000, which is hereby incorporated herein by reference in its entirety.

10 BACKGROUND OF THE INVENTION

The present invention generally relates to the production of a semiconductor grade material. More specifically, the present invention is directed to a process for monitoring the gaseous environment within a crystal puller, such as that employed for single crystal silicon growth, by means of periodic sampling and analysis. Such a process enables the initiation or start-up of the growth process to be more efficiently automated. Additionally, the process enables the early detection of changes in growth process conditions resulting from, for example, a loss of vacuum integrity within the crystal puller or the aging or decomposition of parts within the puller.

Semiconductor material, such as single crystal silicon used for microelectronic circuit fabrication, is typically prepared by the Czochralski (Cz) method. In this process, for example, a single crystal silicon ingot is produced within the crystal growth furnace chamber of a crystal puller by melting a polycrystalline silicon charge in a fused quartz crucible, dipping a seed crystal into the molten silicon, withdrawing the seed crystal to initiate single crystal growth (i.e., forming a neck, crown, shoulder, etc.), and growing the main body of the single crystal under process conditions controlled to maximize the performance characteristics of wafers obtained from the single crystal ingot. In view of the fact that integrated circuit manufacturers continue to place more stringent

limitations upon silicon wafers obtained from these ingots, it is of particular importance to minimize those instances wherein, during ingot growth, the conditions within the crystal puller are not within acceptable ranges or limits. Process control is also important because such "out of process" growth conditions can and do lower the quality of the single crystal silicon produced, which in turn decreases process throughput and overall process efficiency and economy.

Czochralski crystal growth is a batch-wise process in that, after producing one or more crystals, it is necessary to discontinue the growth process in order to open the crystal puller, for example, to clean the furnace and replace and/or recharge the crucible. Each time the crystal furnace is opened, many of the vacuum seals are broken, which increases the chance that one or more seals will not adequately engage to prevent leaks when the furnace is closed to begin a new production cycle. In addition to leaks which may occur as a result of opening the crystal puller, the continuously varying thermal conditions within the puller during a growth cycle result in ever-changing stress levels on the crystal growth chamber walls, observation ports and piping connections. Occasionally, these changing stresses produce conditions that can compromise vacuum seals or create fractures in welds, thus creating additional air, and in some cases water, leaks.

As a result, before a production cycle is begun, it is important to conduct a "pre-fire" vacuum check to determine whether any leaks are present in the crystal puller, or more specifically to determine if any leaks which are out of the ordinary are present, and thus to ensure the vacuum integrity of the crystal growth furnace. A two-step method for testing the vacuum integrity of the crystal growth furnace is commonly employed. The first step involves reducing the pressure within the crystal puller furnace over a set period of time to confirm that the pumping system is

5 working satisfactorily. Then, in the second step, the
furnace is isolated from the vacuum pumping system to
measure how well the furnace holds the vacuum and to
determine whether any leaks which are out of the ordinary
are present; that is, once the pressure is reduced, the rate
at which the vacuum pressure is lost over a period of time
(e.g., 10 minutes) is measured to determine if the rate is
out of the ordinary, thus signaling the presence of an
atypical leak. Although this practice can identify a leak,
10 the procedure requires a significant amount of time to
perform and cannot distinguish the type of leak present or
accurately quantify the amount of a suspect leak in the
furnace. Furthermore, as the use of large diameter furnaces
becomes more prevalent, this practice becomes even less
15 reliable because the large volume of the furnace makes it
more difficult to detect small, but significant, leaks. In
other words, for large pullers, smaller leaks that can
significantly affect the quality of the material being grown
are not easily detected because these leaks do not
20 significantly affect the rate at which a large volume
furnace loses vacuum pressure.

The presence of leaks in the crystal furnace, which may
allow the entry of air and/or water, or water vapor, into
the gas stream above or adjacent to the crystal melt, can
25 result in the loss of crystal puller vacuum integrity, which
in turn leads to "out of process" conditions or problems
during crystal growth. Such "out of process" conditions may
also arise during the growth process because of the natural
deterioration or aging of the crystal puller parts (e.g.,
30 heaters, heat shields, insulation, etc.). Left unchecked,
such conditions can significantly reduce the efficient
production of an acceptable silicon material. For example,
although carbon monoxide is typically present within the
crystal puller during crystal growth (formed, for example,
35 by a reaction between the silicon dioxide crucible and the
graphite susceptor, or between silicon oxide (SiO) given off

from the silicon melt and hot graphite parts in the furnace), elevated carbon monoxide concentrations can result from the presence of air or water vapor within the crystal puller. An elevated carbon monoxide concentration can lead to (i) an elevated carbon level in the crystal that is produced, which is detrimental because this can lead to increased oxygen precipitation in wafers obtained therefrom, and (ii) an increase in the amount of oxide particles formed within the crystal puller, which is detrimental because these oxide particles may accumulate on surfaces within the crystal puller to the extent that flakes may break free and fall into the silicon melt, leading to the loss of dislocation-free growth.

Historically, the loss of vacuum integrity, or the occurrence of "out of process" conditions, has not been reliably monitored or detected *during* crystal growth. Although the occurrence of a large air or water leak may be detected during crystal growth if the crystal puller operator observes an increase in the density of an oxide plume from the silicon melt, and/or an increase in the build-up of silicon oxide on hot zone parts within the operator's view, "out of process" conditions affecting crystal growth are typically not detected until *after* the crystal growth cycle is completed. For example, the presence of a high level of carbon monoxide over the silicon melt surface is typically determined or detected by measuring the amount of carbon in the latter portion of the single crystal silicon ingot. Accordingly, if a problem exists, it is not discovered until after an unacceptable product has been made. In fact, because there can be significant time delays before a defectively-grown ingot is sampled and tested, and the results communicated to the operator of the crystal puller, growth of a second unacceptable ingot can occur. As a result, *multiple* defective ingots can be grown before an unacceptable process

condition is identified, resulting in lost resources,
decreased throughput and increased waste.

Accordingly, a need continues to exist for a process by
which the gaseous environment within a crystal puller can be
more efficiently monitored. More specifically, a need
exists for the means by which to more efficiently (i)
conduct pre-fire vacuum integrity tests and (ii) detect
atypical changes in the vacuum integrity and/or the growth
conditions within the crystal growth chamber *during* the
crystal growth process. Preferably, such a process would
provide for the automatic start-up of ingot growth if
conditions (e.g., vacuum integrity) are acceptable for
successful crystal growth, and further would provide for the
real time notification of the crystal puller operator when
an unacceptable growth condition arises. Such an approach
would thus enable the crystal growth process to be altered,
or aborted, before or during crystal growth, thus limiting
waste and increasing throughput or yield.

Summary of the Invention

Among the several features of the invention, therefore,
may be noted the provision of a process for monitoring the
gaseous environment within a crystal puller before and/or
during semiconductor growth; the provision of such a process
wherein vacuum integrity is monitored by means of sampling
and analyzing the gaseous environment within the crystal
puller; the provision of such a process wherein an
atmosphere over the melt and/or the exhaust from the crystal
puller is sampled and analyzed; the provision of such a
process wherein the start-up of the crystal growth process
is automated; the provision of such a process wherein an
atypical leak is detected and characterized (as, for
example, an air leak, a water leak or a purge gas leak); the
provision of such a process wherein the size and location of
an atypical leak are characterized and quantified; the
provision of such a process wherein real-time feedback of

the gaseous atmosphere and/or exhaust are provided to an operator of the crystal puller; the provision of such a process wherein elevated levels of carbon monoxide are indicated during crystal growth; and, the provision of such a process wherein throughput and yield for a given crystal puller are increased.

Briefly, therefore, the present invention is directed to a process for monitoring the gaseous environment within a sealed crystal pulling furnace, used for the growth of an ingot of a semiconductor material in a growth chamber maintained at a sub-atmospheric pressure. The process comprises sealing the chamber, reducing the pressure within the sealed chamber to a sub-atmospheric level, introducing a process gas into the chamber to purge the chamber and form a gaseous environment therein, and analyzing the gaseous environment within the chamber for the presence of a contaminant gas in a concentration which is greater than the concentration of said gas in the process gas.

Further, the present invention is also directed to a system for use in combination with an apparatus for growing a semiconductor ingot, wherein the semiconductor growing apparatus has a growth chamber maintained at a sub-atmospheric pressure and containing a gaseous environment comprising a process purge gas. The system comprises a port for withdrawing a sample of the gaseous environment from the growth chamber; a detector for analyzing the sample for a contaminant gas in a concentration in excess of the concentration of the gas in the process purge gas and generating a signal representative of the detected concentration of the contaminant gas, wherein the detector receives the sample from the growth chamber via a conduit connected to the port; and a control circuit receiving and responsive to the signal generated by the detector for determining if the detected concentration of the contaminant gas exceeds a pre-set threshold concentration for the contaminant gas, wherein the control circuit controls the

semiconductor growth apparatus in response to the determination.

Other objects and features of the present invention will be in part apparent and in part pointed out hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a section view of the right side of a Czochralski crystal growth furnace chamber.

Fig. 1B is a section view of the left side of a Czochralski crystal growth furnace chamber.

Fig. 2 is a schematic diagram of one embodiment of a system for quantifying, monitoring and/or controlling growth of a semiconductor material in a Czochralski crystal growth furnace chamber.

Fig. 3 is a graph showing the measured carbon monoxide concentrations for the crystal growth runs A through S, as described further in Example 2.

Fig. 4 is a graph comparing the measured carbon monoxide concentrations within the furnace and exhaust gases for the crystal growth runs A through S, as described further in Example 2.

Fig. 5 is a graph showing the measured carbon concentrations of some of the crystals produced in the crystal growth runs described in Example 2.

Figs. 6a and 6b are copies of photographs taken of two ingots, grown as described in Example 2, while Fig. 6c is a copy of a photomicrograph of a segment of the ingot shown in Fig. 6b.

Fig. 7 is a graph showing the measured nitrogen concentrations within the crystal furnace gases during the pre-fire check before crystal growth runs A through P, as described further in Example 3.

Fig. 8 is a graph showing the measured nitrogen concentrations within the crystal furnace exhaust gases

during the pre-fire check before crystal growth runs A through P, as described further in Example 3.

Fig. 9 is a graph showing the measured nitrogen concentrations within the crystal furnace gases during the crystal growth runs A through P, as described further in Example 3.

Fig. 10 is a graph showing the measured nitrogen concentrations within the crystal furnace exhaust gases during the crystal growth runs A through P, as described further in Example 3.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the process of the present invention, it has been discovered that the gaseous environment within a crystal puller can be monitored by means of sampling and analyzing that environment to detect: (i) a loss of vacuum integrity, or a change therein, prior to or during the growth of a semiconductor material; and/or (ii) the occurrence of "out of process" growth conditions during the growth of a semiconductor material. More specifically, the present invention monitors the gaseous environment within the growth furnace of a crystal pulling apparatus and/or the exhaust ports of the furnace, in order to identify the presence of one or more contaminant gases at a concentration which is near to, or in excess of, some unacceptable limit. In this way, the presence of leaks, which can lead to changes in the vacuum integrity of the crystal puller before or during the growth process, and/or changes in process conditions during the growth cycle can be detected. Such an approach can provide the crystal puller operator with real time feedback regarding conditions within the crystal puller environment (e.g., the composition of the gaseous atmosphere above the melt surface or of the crystal puller exhaust) prior to and during crystal growth.

The present process thus allows for the start-up of the crystal growth process to be automated, and further enables

much earlier detection of changes within the crystal puller environment which can lead to unacceptable growth conditions. This early detection provides the crystal puller operator with the opportunity to abort the growth process or, in some cases, to initiate corrective actions, at a much earlier stage, thus limiting the amount of unacceptable silicon which is grown. Additionally, monitoring the crystal growth environment over time enables repairs and routine maintenance to be scheduled and completed much earlier and before an unacceptable condition arises, therefore effectively preventing unnecessary process downtime. As a result, the present invention increases overall process throughput and yield, and therefore overall process efficiency.

In this regard it is to be noted that, as used herein, the phrase "vacuum integrity" refers to the ability of the crystal puller to substantially maintain a typical vacuum pressure prior to and during crystal growth. Stated another way, a crystal puller having "vacuum integrity" is substantially free of atypical leaks in the vacuum seals present therein, leaks which would otherwise result in an increase in the concentration of contaminant gases, from the atmosphere outside the crystal puller, beyond acceptable levels (as further described herein). While the "typical" vacuum integrity, or vacuum pressure, may vary from one crystal puller to the next, this is routinely determined by means common in the art, such as by statistical process control ("SPC"), as further described herein below.

It is to be further noted that, as used herein, the term "out of process" refers to a process condition that is atypical, unexpected, or out of the ordinary. Again, while such conditions may vary from one crystal puller or crystal pulling process to another, "in process" conditions are routinely determined by means common in the art, such as by statistical process control. Examples of such "out of process" conditions include when an upper or lower control

limit, as established by SPC, is exceeded, or when a process condition, over a statistically significant number of monitoring cycles, appears to be trending away from what is typical.

5 It is to be still further noted that, as used herein, "real time" is intended to refer to a process wherein sampling, analysis, and the reporting of results occur essentially instantaneously; that is, there is essentially no delay in the time (i.e., less than about 1 second, 0.5
10 seconds, or even 0.2 seconds) over which samples are collected, analyzed and reported to the operator. As a result, there is essentially no difference between the gaseous environment within the puller at the time the samples are collected and at the time the results are
15 reported.

System Design Overview

 The present invention will be described within the context of an exemplary crystal pulling apparatus suitable for the growth of semiconductor material. More
20 specifically, the present invention will be generally described within the context of a Czochralski-type crystal growth furnace, such as that commercially available from Kayex of Rochester, NY, designed for the growth of a 300 mm nominal diameter single crystal silicon ingot. However, in
25 this regard, it is to be noted that the invention may likewise be used with any Czochralski-type furnace design suitable for the growth of various diameters (e.g., nominal diameters of 150 mm, 200 mm and 300 mm or more) of silicon and other such semiconductor materials, such as compound
30 semiconductors (e.g., GaAs).

 Referring now to Figures 1A and 1B, the crystal growth furnace, sealed with the crystal pulling apparatus, comprises a pulling chamber 50 having a device (not shown) for lifting and rotating a growing crystal 55, a growth
35 chamber 51 wherein the polysilicon charge is melted in a

silica crucible 56 supported by a graphite susceptor 57 and heated by an electrical resistance graphite heater (not shown). The furnace further comprises a purge tube 60 wherein an inert purge gas 58, such as argon, preferably
5 flows down the center of the crystal puller 50, over the growing silicon ingot 55 and is predominantly peripherally constrained by the inner surface 61 of the vertical wall 62 of the purge tube 60. The purge gas 58 mixes with SiO over the melt surface 53 and the gas mixture flows peripherally
10 outward and then upward through an annular region 59 defined by the outside surface 63 of the purge tube vertical wall 62 and the inner wall surface 57 of the crucible 56. The gas mixture exiting the annular region 59 as well as purge gas 58 that was not constrained by the purge tube 60 is removed
15 from the crystal puller 50 via four exhaust outlets 64a, 64b, 64c and 64d arranged so as to be equidistant along the periphery of the base of the growth chamber. The exhaust outlets 64a through 64d are in fluid communication with a vacuum pumping system 70 by a vacuum piping system
20 comprising two pairs of vacuum pipes 71a and 71b. Each pair of vacuum pipes is attached to two of the exhaust outlets 64a through 64d and extend into the growth chamber 51 by graphite extensions lined with silica glass tubes (not shown). Each pair of vacuum pipes 71a and 71b are reduced
25 into a right-hand side (RHS) pipe 72 and a left-hand side (LHS) pipe 73 respectively. The RHS pipe 72 and LHS pipe 73 are subsequently reduced into a main exhaust pipe 76, which ends into the vacuum pumping system 70. A main exhaust valve 77 is positioned in the main exhaust pipe 76 prior to
30 the vacuum pumping system 70.

In operation, the present process samples the gaseous environment from within the growth furnace, for example, the atmosphere above the melt surface and/or the gases in the exhaust from the crystal pulling furnace chamber, and passes
35 the samples to a detector for characterization and/or quantification. More specifically, in the context of the

embodiment shown in Figures 1A and 1B, samples of the gas above the melt (referred to herein as Port 1 samples) are collected from one or more sample ports 10 positioned adjacent to the growing crystal 55 within the crystal puller and samples of the gas in the furnace exhaust (referred to herein as Port 2 and Port 3 samples) are collected from sample ports 74 and 75 located within exhaust pipes 71a and 71b respectively.

In this regard it is to be noted that the position of the sampling ports may be other than herein described. For example, generally speaking, the ports are positioned at locations which enable collection of the most representative samples of gases which the melt surface and growing ingot "encounter." Additionally, it is to be noted that, although preferred in some embodiments, the sampling and analysis of exhaust gases are optional. Experience to-date indicates sampling in this location can be beneficial, for example, in characterizing the source or cause of "out of process" growth conditions in the growth chamber.

It is to be further noted that, depending on the diameter of the crystal puller and/or other dimensions of the crystal growth furnace, it may be preferable to monitor the gases from within the crystal growth furnace at more than one sample port 10, particularly when gas flow within the chamber is not uniform above the melt. In any case, when positioning sample port(s) 10 within the growth furnace, the sample port(s) is preferably located sufficiently far from the direct flow of purge gas 58 or any known sources of common air leaks (for example, the polysilicon feed tube), such that the collected samples are not diluted or would otherwise not be representative of the gaseous environment adjacent to the growing crystal. In a particularly preferred embodiment, sample port 10 is positioned above the section of the purge tube 60 wherein the flow of purge gas 58 is not constrained within the purge tube 60 as described above. This is preferable, for

example, because the flow of purge gas in this region tends to develop eddys 65 which, over time, may further concentrate any contaminant gases which may be present above the crystal melt before such gases can be delivered to the furnace exhaust. Therefore, in this sense, samples collected from this "eddy region" may be more likely to indicate a loss of vacuum integrity or other out of process condition.

Referring now to Figure 2, the collected samples are passed from the sample ports (sample port 10, sample port 74 and sample port 75) to the detector 100 through individual conduits 90, which typically comprise one-quarter inch (about 6 mm) diameter flexible stainless steel tubes, which may optionally be wrapped in heating tape (not shown) in order to prevent the condensation of gases. The conduits 90 are in fluid communication with the sample ports 10, 74 and 75 and are adapted for fluid communication with the detector 100. While the sample ports may be directly connected to the detector 100, sample transfer is preferably facilitated by means of a sample transfer device 91 or other means for connecting and switching between multiple sample inlets.

The transfer of gases from the sample ports to the detector 100 may be further facilitated by means of a vacuum pump 92 having a suction line 93 in fluid communication with the conduit 90 or sample transfer device 91. The vacuum pump 92 should preferably be capable of drawing a vacuum of less than about 10 torr (about 1.5 Pa). The suction line 93 can draw from conduit 90 or sample transfer device 91 to pass a sample to the detector 100. The suction line 93 preferably draws from the sample transfer device 91 between first and second detector sample orifices 94, 95 which regulate the sample flow rate to the detector 100. While a single sample orifice configuration can be used, in some embodiments the double sample orifice configuration depicted in Figure 2 is a preferred system for pressure reduction and is preferably used in conjunction with a continuous flow

sample stream bypass. The pressure between the first and second sample orifices 94, 95 is preferably maintained at about 500 mtorr (about 65 Pa) to provide a sufficient pressure differential to transfer the detector sample from the sample port 10 through the conduit 90 to the detector 100. An orifice size of about 1 μm can be used in the second sample orifice 95. The size of the first sample orifice is not narrowly critical, but preferably ranges from about 10 μm to about 5 mm. The sample system is preferably regulated to obtain a constant mass flow rate of gas through the sample port 10 and a constant pressure between the sample orifices 94, 95. Under such conditions, the detector sample enters the detector 100 with a constant volumetric flow rate.

Generally speaking, the sampling system is designed to allow for sampling of the furnace and exhaust gases at temperatures and pressures common for Cz-types of single crystal silicon growth processes, by means of commercially available atmospheric sampling valves. Typically, however, the pressure within the crystal puller during sample collection ranges from about 2 to about 50 torr, from about 5 to about 40 torr, or even from about 10 to about 30 torr, while the temperature ranges from about ambient temperature to about 1400°C (or more, given that "hot spots" within the growth chamber can occur in some areas, at times reaching 1500°C, 1600°C, or even 1700°C). More specifically, suitable detectors 100 for monitoring the composition of the gaseous atmosphere above the melt or the exhaust gases from the crystal growth chamber, and/or quantifying the amount of a particular gas therein, include commercially available mass analyzers and gas chromatographic detectors, with mass analyzers being preferred in some embodiments. A particularly preferred detector is a closed (or enclosed) ion source quadrupole gas mass analyzer, having a mass range of about 1 to about 100 amu and a minimum detectable partial pressure of about 5×10^{-14} torr (using an electron multiplier

detector). Such a gas mass analyzer typically operates at pressures ranging from about 1×10^{-4} torr (1.3×10^{-2} Pa) to about 1×10^{-2} torr (1.3 Pa) in their ionizing section, and at pressures ranging from about 1×10^{-6} torr (1.3×10^{-4} Pa) to about 1×10^{-4} torr (1.3×10^{-2} Pa) in their detecting section. An example of a suitable detector is a residual gas analyzer (RGA) such as a Qualitorr Orion Quadrupole Gas Mass Analyzer System (available from MKS, UTI Division of Walpole, Massachusetts).

The detector is preferably adapted to detect and quantify the amount of a contaminant gas (e.g., nitrogen, oxygen, water vapor, carbon monoxide) within the collected sample, and thus within the gaseous environment from which the sample was obtained. Additionally, a process purge gas (e.g., argon) is sampled, particularly as a standard to quantify the amounts of the other gases present. For example, in a particularly preferred embodiment wherein the detector is a RGA as described above, it is preferred to monitor N_2 at 14 atomic mass units (amu), monitor O_2 at 32 amu, monitor H_2O at 17 amu, monitor CO at 28 amu and monitor Argon by measuring Ar isotope 36 at 36 amu. As used herein, atomic mass units are equivalent to the particular species molecular weight divided by the charge on the molecule, with the charge on the molecule determined by the ionizer in the RGA. The ionizer may also crack or doubly charge the molecules upon entering the RGA. In any case, the amu for each species of interest should be selected so as to reduce any interference between other major species in the furnace and exhaust gases. In this regard, it has been found to preferably monitor for the presence of H_2O at 17 amu rather than 18 amu to reduce any possible interference with doubly-charged Argon 36. Likewise it is important to note the presence of N_2 at 14 amu to determine if CO should be monitored at 28 amu. If N_2 is present at 14 amu, it is important to look for C at 12 amu to detect the presence of CO so as to minimize any interference with N_2 at 28 amu.

The detector 100 communicates with a PLC or PC furnace control system by means common in the art, such as through a system of open and closed switches or through RS232 or RS485 serial ports. The detector can be instructed by the PLC or PC furnace control system to monitor the gases at desired times and locations (as described herein). The detector 100 outputs a detector signal (e.g., electrical current, voltage, etc.) which is physically representative of, corresponds to or can be correlated to the amount of a particular gas in the furnace chamber or furnace exhaust sample. The detector signal output is communicated, directly or indirectly, to the microprocessor 200. The microprocessor 200 may monitor, display, record or further process the detector signal. In the particularly preferred embodiment wherein the detector is an RGA as described above, the detector signal is converted in the microprocessor to equivalent partial pressures or concentrations of the sampled gases, for example, as follows:

$$N_2 \text{ (ppmv)} = 0.042 \times I^{14 \text{ amu}} / I^{36 \text{ amu}} \times 1,000,000 \text{ ppmv}$$

$$O_2 \text{ (ppmv)} = 0.0034 \times I^{32 \text{ amu}} / I^{36 \text{ amu}} \times 1,000,000 \text{ ppmv}$$

$$H_2O \text{ (ppmv)} = 0.01478 \times I^{17 \text{ amu}} / I^{36 \text{ amu}} \times 1,000,000 \text{ ppmv},$$

$$CO \text{ (ppmv)} = 0.0034 \times I^{28 \text{ amu}} / I^{36 \text{ amu}} \times 1,000,000 \text{ ppmv}$$

where $I^{xx \text{ amu}}$ is the current measured by the RGA detector at $xx \text{ amu}$.

Preferably, the detector signal is transmitted or otherwise communicated, directly or indirectly (e.g., through a microprocessor 200), to a controller 300. Any standard controller may be employed, including, for example, analog proportional (P), proportional-integral (PI) or proportional-integral-derivative (PID) controllers, digital

5 controllers approximating such analog P, PI or PID
controllers, or more sophisticated digital controllers. A
digital PID controller is preferred. Such a digital
controller 300 can itself comprise a microprocessor, or can
comprise a portion of a larger microprocessor 200. The
controller 300 may also communicate, directly or indirectly,
with a separate microprocessor 200 to provide user input to
the controller, data collection, alarm indications, process
control tracking, etc. The controller 300 (or
10 microprocessor 200) may modify the received detector signal
for use in calculating the changes in process conditions,
for user-interface or for data acquisition or display.

15 The controller 300 generates a control signal based on
the detector signal (either as received from the detector
100 or as modified by the microprocessor 200 or controller
300). In a preferred application, the controller converts
the detector signal to a control signal by applying a
control law based upon the conditions necessary for
controlling the automatic start-up of the crystal furnace
20 heater. Generally, this control law may be based on
theoretical and/or empirical considerations. The control
law used in a particular situation varies depending on the
process condition and on the type of process control element
being manipulated. The control signal generated by the
25 controller 300 may be of a variety of types (e.g., pneumatic
or electrical), and can be transmitted or otherwise
communicated, directly or indirectly, to a process control
element 400 which changes at least one process condition. A
control signal can also be communicated to the process
30 control element 400 via the microprocessor 200 (dashed line
in Fig. 2).

35 In view of the foregoing, the present invention will be
discussed hereafter in particular detail in regard to
operating protocols associated with conducting an automated
pre-fire vacuum integrity test and for general monitoring
during crystal growth to detect out of process conditions.

5 It is to be noted, however, that the process of the present invention may be carried out using a system design other than herein described. For example, multiple crystal pullers may be connected to a single RGA monitoring system (e.g., 2, 3, 4 or more).

Pre-Fire Vacuum Integrity Check

10 In the practice of one embodiment of the present invention, the crystal growth process is begun by loading a crucible, contained within a growth furnace or chamber of a crystal pulling apparatus, with an initial charge of a semiconductor raw material (e.g., chunk and/or granular polysilicon) and attaching a seed crystal to the crystal pulling system. The furnace is then closed and sealed. The furnace control system is instructed to begin the pre-fire vacuum check. The inert purge gas (e.g., argon) inlets are closed and the main exhaust valve is opened and the air is pumped from the furnace. When the pressure has been sufficiently reduced, typically to a pressure of less than about 200 mtorr (e.g., about 190, 170, 150 torr or less), the main exhaust valve is closed, the purge inlet is opened and the furnace is filled with a process purge gas, for example argon (Ar), to a pressure of about 100 torr (e.g., about 75, 85, 95, 105, 115 or about 125 torr). The cycle of reducing the pressure and then back-filling with an inert process gas is repeated about two additional times. After the third cycle, the furnace is back-filled to a pressure ranging from about 2 to about 50 torr (e.g., about 5, 10, 15, 20, 25 torr or more), and the process gas inlets and main exhaust valves are balanced to maintain a flow rate ranging from about 15 to about 100 slm (standard liters per minute or liters per minute adjusted for standard temperature and pressure), typically about 20, 40, 60 or even about 80 slm, through the pull chamber, the growth chamber and the exhaust piping.

Generally speaking, once the growth chamber has been sufficiently purged, the gaseous environment is sampled and analyzed about once every 20 minutes, 15 minutes, 10 minutes, 5 minutes or even every minute. Preferably, however, sampling and analysis will occur on a continuous basis. In a particularly preferred embodiment, this is achieved by automated means. For example, when automated, the furnace control system instructs the detector to monitor the gaseous environment within the crystal puller (e.g., the atmosphere over the silicon melt and/or the crystal puller exhaust) at each port (sequentially or, depending upon the number of detectors and/or the system configuration, simultaneously). If the partial pressure of one or more, and typically if the partial pressure of all, contaminant gases of interest (e.g., N_2 , O_2 and/or H_2O) are below an acceptable limit, or alternatively within an acceptable range, the furnace control system allows the heaters in the growth chamber to be energized in order to begin heating/melting the polysilicon charge. Generally speaking, this "pre-fire" check may last a few minutes (e.g., about 2, 4, 8, 10 minutes or more), a few tens of minutes (e.g., about 10, 20, 30, 40 minutes), or more with sample collection and analysis continuing throughout this time frame, or over only a portion thereof.

The sampling and analysis of the gaseous environment will generally continue until it has been determined that it is suitable for crystal growth to be initiated (i.e., for the furnace heater(s) to be "fired"). Based upon experience to-date, it has been found that the furnace heater may typically be started automatically when the gaseous environment within the growth chamber above and/or adjacent to the crucible (Port 1) has a contaminant gas concentration, for example, of less than about 100 ppmv of N_2 (e.g., less than about 80 ppmv, 60 ppmv, 40 ppmv, or even 20 ppmv); less than about 30 ppmv of O_2 (e.g., 25 ppmv, 20 ppmv, 15 ppmv, or even 10 ppmv); and/or, less than about 200 ppmv

of H₂O (e.g., 175 ppmv, 150 ppmv, 125 ppmv, or even 100 ppmv). However, in those instances where the concentration of a contaminant gas is in excess of the noted limit (i.e., the automatic starting values), the crystal furnace operator may optionally override the monitoring system and manually start the crystal furnace heater. For example, such actions may be taken when the concentration of N₂ ranges from about 100 to about 600 ppmv (e.g., from about 150 to 550 ppmv, about 200 to about 500 ppmv, or about 250 to 450 ppmv), the concentration of O₂ ranges from about 30 to about 100 ppmv (e.g., from about 40 to 90 ppmv, or about 50 to 80 ppmv), and the concentration of H₂O ranges from about 200 to about 1000 ppmv (e.g., from about 300 to 900 ppmv, about 400 to 800 ppmv, or about 500 to 700 ppmv). For concentrations of N₂ above about 600 ppmv, O₂ above about 100 ppmv, and H₂O above about 1000 ppmv, the furnace control system will typically require restarting the pre-fire vacuum check.

Although optional in some embodiments, when exhaust sampling is employed (e.g., from the RHS pipe (Port 2) and the LHS pipe (Port 3)), the furnace control system will typically start the furnace heater automatically if the concentration of N₂ is less than about 50 ppmv (e.g., less than about 40, 30, or even 20 ppmv), the concentration of O₂ is less than about 10 ppmv (e.g., less than about 8, 6 or even 4 ppmv), and the concentration of H₂O is less than about 200 ppmv (e.g., less than about 175 ppmv, 150 ppmv, 125 ppmv, or even 100 ppmv). For concentrations exceeding these automatic starting values, the crystal furnace operator may override the monitoring system and manually start the crystal furnace heater when the concentration of N₂ ranges from about 50 to about 100 ppmv (e.g., from about 60 to 90 ppmv, or about 70 to 80 ppmv), the concentration of O₂ ranges from about 10 to about 20 ppmv (e.g., from about 12 to 18 ppmv, or about 14 to 16 ppmv), and the concentration of H₂O ranges from about 200 to about 1000 ppmv (e.g., from about 300 to 900 ppmv, about 400 to 800 ppmv, or about 500 to 700

ppmv). For concentrations of N_2 above 100 ppmv, O_2 above 20 ppmv and H_2O above 1000 ppmv, the furnace control system will typically require restarting the pre-fire vacuum check.

5 In this regard it is to be noted that, in some instances, the initial water concentration (i.e., the water concentration prior to the "firing" of the heaters) may be ignored; that is, in some instances, the growth process may be initiated when the water vapor concentration is in excess of 1000 ppmv. Generally speaking, this is because, in a
10 crystal puller at ambient temperature, a significant amount of water vapor can be present on, for example, the surfaces of the graphite parts. Given that the puller is rapidly heated to a temperature in excess of that which causes water to vaporize, this initial presence of water can be quickly
15 reduced.

It is to be further noted that, in some instances, the vacuum integrity of the crystal puller is monitored by means of analyzing the gaseous environment within the crystal
20 puller for the presence of all of the above-referenced contaminant gases, while in other instances the environment will be analyzed for the presence of only one or two of the gases. Additionally, it is to be noted that the inert process or purge gas employed may contain trace levels of one or more of the contaminant gases, levels which are
25 acceptable for purposes of the present invention.

Accordingly, generally speaking, the process of the present invention enables the *automated* "firing" of the crystal
30 puller when the concentration of nitrogen ranges from about 5 ppmv to less than about 50 ppmv or 100 ppmv (depending upon whether the concentration in the exhaust gas or above/adjacent to the melt surface, respectively, are being considered), when the concentration of oxygen ranges from about 2 ppmv to less than about 10 ppmv or 30 ppmv (again, depending upon whether the concentration in the exhaust gas
35 or above/adjacent to the melt surface, respectively, are

being considered), and when the concentration of water ranges from about 2 ppmv to less than about 200 ppmv.

5 It is to be still further noted that while the concentration levels provided above are generally applicable to semiconductor growth processes, the "critical" levels for
10 initiating growth may be other than described herein without departing from the present invention. Specifically, from one crystal puller or crystal pulling process to another, the unacceptable level of one or more contaminant gases may vary. As a result, it is preferred to employ means common
15 in the art, such as statistical process control, to determine a "baseline" for each process condition or contaminant gas level which is "typical." Such an approach generally involves conducting a series of pre-fire tests, and optionally a series of complete growth cycles, while
20 monitoring the growth conditions in order to identify typical or ordinary conditions. A "window" of acceptable conditions is then established; that is, some degree of variation (e.g., about 2%, 4%, 6%, 8%, 10%, etc.) is then allowed, beyond which the crystal puller operator is notified that an atypical condition is present. A common approach, for example, is to conduct a series of statistically significant tests to establish a median level for each contaminant gas of interest, and then allow a range
25 of: (i) median plus, or in some cases minus, two times the standard deviation, (ii) median plus, or in some cases minus, three times the standard deviation, or (iii) median plus, or in some cases minus, some multiple of the standard deviation in excess of three (e.g., 4, 5 or more). In this
30 way, the present process may be "tuned" to optimize the pre-fire or growth conditions for any crystal puller or crystal pulling process.

35 In a preferred embodiment, the concentration of a contaminant gas is determined at multiple locations (e.g., above and/or adjacent to the melt surface and/or in one or more of the exhaust gas ports), before the heaters of the

5 crystal puller are "fired" and meltdown is begun. As
discussed further below, sampling in multiple locations is
beneficial for a number of reasons. For example, depending
upon design of the growth chamber, gas flow through the
chamber may not be uniform. As a result, regions having
different gas compositions within the chamber may be
present. Additionally, the vacuum integrity of the crystal
puller may be compromised in a number of different ways,
each of which may occur in a localized area, again depending
10 upon the design of the crystal puller/crystal growth
chamber. These factors should be kept in mind when
optimizing (either by empirical means, or by gas flow models
common in the art) sample port placement, the number of
sample ports to be employed, sampling frequency, etc.

15 ***Monitoring During Crystal Growth***

In a second embodiment of the present invention, during
the semiconductor growth process (i.e., once meltdown has
begun), gases within the growth chamber above and/or
adjacent to the silicon melt surface, and/or the gases in
20 the exhaust from the chamber, are periodically sampled and
analyzed, in order to monitor the vacuum integrity of the
crystal puller, as well as to monitor the growth chamber for
the presence of other problems which may develop during the
growth process (e.g., failure of a purge gas valve, break or
25 leak in a water jacket, build-up of carbon monoxide
resulting from the reaction between silicon oxide with
various graphite parts, etc.). The gaseous environment with
the growth chamber is sampled and analyzed for the presence
of a contaminant gas (e.g., oxygen, nitrogen, water vapor,
30 carbon monoxide) in a concentration in excess of some
predetermined limit.

The timing of sample collection (e.g., when sampling
begins, ends, duration between each sample taken, the number
of samples taken during the process, etc.), as well as the
35 location and number of sampling points, will generally be

that which is sufficient to ensure representative data of the crystal puller environment is provided throughout the growth process. More specifically, however, sampling for this phase of the present process typically begins as soon as the heaters have been "fired" and initiation of the meltdown has begun, in order to ensure no leaks are present prior to initiation of the semiconductor growth process. Sampling can continue throughout the entire course of crystal growth (e.g., from initiation of meltdown until the end-cone is detached from the melt, or even longer, such as until cool-down of the puller has occurred). Alternatively, sampling may occur over only a portion of this time frame (e.g., during meltdown, growth of the neck or crown, growth of about 20%, 40%, 60%, 80% or about all of the main body, growth of the end-cone, etc.). Regardless of the time frame over which sampling occurs, during the growth process, sample collection and analysis typically occurs at Port 1, and optionally at Ports 2 and 3, about once every 20 minutes, 15 minutes, 10 minutes, 5 minutes, or every minute, or even on a continuous basis.

In this regard it is to be noted that the timing for sampling may be other than herein described without departing from the scope of the present invention. For example, sample collection/analysis may vary depending upon the growth conditions employed, the type of semiconductor material to be formed, the design of the crystal pull apparatus, etc. Generally speaking, however, the timing for a given puller, process, type, etc. may be optimized empirically, for example, by growing a number of different crystals and varying the point at which sample collection begins and ends, how often samples are taken, the number of samples taken, etc.

Generally speaking, when the presence of a contaminant gas is detected at a concentration in excess of the "background" concentration (i.e., at a concentration in excess of the typical concentration, as described further

herein, such as the concentration at which the particular
contaminant gas of interest is present in the process or
purge gas being used), or alternatively when it is detected
at a concentration at or nearing some unacceptable
concentration, the growth process can be halted, in order to
avoid the growth of a segment of a semiconductor ingot
(e.g., single crystal silicon ingot) that is not suitable
for use. In such cases, the grown ingot can be further
processed without concern of an unacceptable segment being
present, as the result of an "out of process" condition or
an atypical crystal puller leak. The crystal puller can
then be immediately examined to identify the source of the
contaminant gas, thus limiting "down time" for the crystal
puller.

Additionally, if the "out of process" contaminant level
is set sufficiently low, the growth process can be continued
while the gas level is monitored until just before a
"critical" level is reached, at which point growth must be
halted to prevent the formation of an unacceptable material.
In such instances, corrective actions may be attempted,
(e.g., the source of the leak may be located and repaired)
during the growth process. Alternatively, other attempts
can be taken to prolong the growth cycle, such as, for
example, by increasing the flow of an inert purge gas into
the crystal puller and/or thereby increasing the flow of
exhaust gas out of the crystal puller. In this way, the
concentration of the contaminant gas can be diluted or
suppressed for a period of time.

In accordance with the process of the present invention,
losses in the vacuum integrity of the crystal growth chamber
(such as by leaks), and additionally changes in process
conditions (i.e., "out of process" conditions) resulting
from other sources (e.g., silicon oxide reacting with
graphite parts within the growth chamber), are detected by
closely monitoring, and preferably continuously monitoring,
the composition of the gaseous environment within the

5 chamber, and/or the composition of the exhaust gases from
the chamber. More specifically, as described above, after
the crystal puller is sealed, the pressure therein is
reduced and the sealed chamber is repeatedly purged with an
inert process or purge gas in order to lower the
concentration of contaminant gases to below some acceptable
level. For example, the system may be purged to lower the
concentration of nitrogen to less than about 600 ppmv, 400
ppmv, 200 ppmv, or even 100 ppmv; to lower the concentration
10 of oxygen to less than about 100 ppmv, 90 ppmv, 60 ppmv, or
even 30 ppmv; and to lower the concentration of water to
less than about 1000 ppmv, 800 ppmv, 600 ppmv, 400 ppmv or
even 200 ppmv. Once this has been achieved, and the silicon
meltdown and/or ingot growth has begun, the gaseous
15 environment within the crystal puller will be monitored for
gas concentrations in excess of these amounts.

In this regard it is to be noted that the inert process
or purge gas employed may contain trace levels of one or
more of the contaminant gases, levels which are acceptable
20 for purposes of the present invention. Accordingly,
generally speaking, the process of the present invention
allows for ingot growth to continue when the concentration
of nitrogen in the gaseous environment ranges from about 5
ppmv to less than about 600 ppmv (e.g., from about 25 to 400
25 ppmv, about 50 to 200 ppmv, or even about 75 to 100 ppmv),
when the concentration of oxygen ranges from about 2 ppmv to
less than about 100 ppmv (e.g., from about 10 to 90 ppmv,
about 15 to 60 ppmv, or even about 20 to 30 ppmv), and when
the concentration of water vapor ranges from about 2 ppmv to
30 less than about 1000 ppmv (e.g., from about 25 to 800 ppmv,
about 50 to 600 ppmv, about 75 to 400 ppmv, or even about
100 to 200 ppmv).

35 It is to be further noted that, unlike the "pre-fire
check," the gaseous environment is also sampled and analyzed
for the presence of carbon monoxide; that is, because carbon
monoxide begins to form only after the growth chamber is

heated, the concentration of carbon monoxide in the gaseous environment within the crystal puller is a concern only after the "pre-fire check" has been completed. Generally speaking, because carbon monoxide is essentially a by-product of the growth process (e.g., the result of a reaction between the silicon dioxide crucible and the graphite susceptor), the gaseous environment will be monitored for a concentration which is in excess of a "background" concentration, with corrective action being taken or the growth process being halted when concentrations that would result in "carbon doping" of the melt occur. Although the concentration will vary with the location of the sampling port P1 (i.e., the port sampling the atmosphere above or adjacent the melt), the "background" concentration of carbon monoxide typically ranges from a few ppmv (e.g., about 2, 4, 6, 8, 10 ppmv or more) to several ppmv (e.g., about 15, 20, 25, 30 ppmv or more). In contrast, carbon monoxide concentrations below the melt (i.e., in the lower regions of the crystal growth chamber, generally below the crucible) are typically quite higher. Thus, the concentration of carbon monoxide in the exhaust port samples will typically be several tens of ppmv (e.g., about 20, 40, 60, 80, 100 ppmv or more). Just as melt doping can be a concern when the carbon monoxide concentration above the melt is elevated (e.g., at concentrations in excess of about 30 or 40 ppmv), elevated concentrations below the melt (e.g., at concentrations in excess of about 100 or 150 ppmv) can be a strong indication of problems within the pull chamber (such as a water leak below the crucible), even when the concentration above the melt is not out of the ordinary or is below an acceptable limit. Such information is beneficial, for example, in more precisely determining when crystal puller maintenance is needed.

It is to be still further noted that while the concentration levels provided above are generally applicable to semiconductor growth processes, the "critical" levels for

the growth process may be other than described herein without departing from the present invention. Specifically, from one crystal puller or crystal pulling process to another, the unacceptable level of one or more contaminant gases may vary. As a result, it is preferred to employ means common in the art, such as statistical process control, to determine a "baseline" for each process condition or contaminant gas level which is "typical." Such an approach generally involves conducting a series of growth cycles, while monitoring the growth conditions in order to identify typical or ordinary conditions. A "window" of acceptable conditions is then established; that is, some degree of variation (e.g., about 2%, 4%, 6%, 8%, 10%, etc.) is then allowed, beyond which the crystal puller operator is notified that an atypical condition is present. A common approach, for example, is to conduct a series of statistically significant tests to establish a median level for each contaminant gas of interest, and then allow a range of: (i) median plus, or in some cases minus, two times the standard deviation, (ii) median plus, or in some cases minus, three times the standard deviation, or (iii) median plus, or in some cases minus, some multiple of the standard deviation in excess of three. In this way, the present process may be "tuned" to optimize the growth conditions for any crystal puller or crystal pulling process.

Such an approach is advantageous for a number of reasons. For example, the particular gas or gases of concern may vary depending upon, for example, the type of material being grown, the type of crystal puller, the location of the crystal puller, the source or type of process purge gas being employed, etc. Growth conditions can also be a factor. For example, higher growth temperatures tend to cause higher "typical" levels of carbon monoxide in the crystal puller (higher temperatures increase the rate of those reactions which produce it). As a result, a higher process temperature means a higher overall "in

process" level of carbon monoxide is acceptable, in comparison to when a lower process temperature is employed.

Identification of the Type and/or Source of Leak

5 It is to be noted that the process of the present invention is advantageous over methods commonly employed in semiconductor growth processes for a number of reasons. For example, not only does the present invention enable the time for "pre-fire" testing to be reduced, as well as enabling the early detection of contaminant gases in the crystal
10 puller, but it also provides information regarding the nature of the leak or contaminant source within the puller. For example, if only nitrogen is found to be at elevated levels, one might suspect that the purge gas is contaminated, because an air leak would lead to the presence
15 of oxygen, and probably water vapor, as well. Similarly, if only water vapor is detected at elevated levels, one might suspect a water leak, because an air leak would lead to the presence of nitrogen, as well. In this way the present invention may act to further reduce equipment "down time,"
20 because the potential sources of the problem can be prioritized.

25 Additionally, the location of the port from which samples are collected, as well as the timing of the analysis of those samples, can also be controlled to provide beneficial information. For example, sampling and analyzing the exhaust gases is often preferred in some embodiments because the results, when compared to the results of samples collected above the melt or adjacent to the growing ingot, may help to identify the potential cause of an "out of
30 process" condition or to perform "trouble shooting" to determine if other problems with the puller exist (e.g., problems which do not result in "out of process" conditions). For example, by monitoring the exhaust gases in addition to the gases above the melt or adjacent to the
35 growing ingot,

1. the cause of an elevated carbon monoxide level (as detected by port(s) 2 and/or 3) might be identified as being caused by a bad heater (i.e., a heater having "hot spots" which increase the reaction between SiO in the gaseous environment and carbon from the graphite heater), if the samples collected and analyzed above the melt show no indication of an oxygen leak; or,
2. the cause of an elevated nitrogen level above the melt (as detected by port 1) in the absence of oxygen or water, might be identified as an air leak near the bottom of the crystal puller furnace, the oxygen being converted to carbon monoxide or silicon dioxide (which might also be detected by sampling at port 1, or alternatively might be swept out of the puller before being detected).

In any event, depending upon the level of the contaminant gas present, pulling may continue while the level is carefully watched and corrective action is taken. In this way, "trouble shooting" may be carried out while semiconductor growth continues. "Trouble shooting" can also be achieved, for example, by comparing the difference between the concentration of a particular contaminant gas at two different locations. In this way one can monitor for the presence of a difference, or an atypical difference, in the concentrations. One beneficial practice is to compare the levels of carbon monoxide present in samples collected at ports 2 and 3. Typically, any difference will be less than about 20 ppmv, 15 ppmv, 10 ppmv, 5 ppmv or even less than about 2 ppmv (with lower differences corresponding to lower "typical" levels of carbon monoxide present in the furnace; e.g., less than about 100 ppmv, 80 ppmv, 60 ppmv, 40 ppmv, 20 ppmv, or less). In this way, problems in the

crystal puller, such as a blocked exhaust outlet, can be detected.

Carbon Content

Substitutional carbon, when present as an impurity in single crystal silicon has the ability to catalyze the formation of oxygen precipitate nucleation centers. Accordingly, in some embodiments, the process of the present invention enables the close monitoring of the gaseous environment within the crystal puller, such that the carbon content of the semiconductor material that is formed has a low concentration of carbon; that is, the semiconductor material typically has a concentration of carbon which is less than about 5×10^{16} atoms/cm³, less than about 1×10^{16} atoms/cm³, or even less than about 5×10^{15} atoms/cm³.

- - - - -

EXAMPLES

The following Examples set forth one approach that may be used to carry out the process of the present invention. Accordingly, these examples should not be interpreted in a limiting sense.

Example 1

This example demonstrates the benefit of conducting an automated pre-fire check in accordance with the method of the present invention to test the vacuum integrity of the crystal puller prior to beginning the crystal growth process.

A crystal process development run was begun by loading a crucible with an initial charge of polysilicon and attaching a seed crystal to the crystal pulling system contained within a 300 mm Cz crystal growth furnace as described in Figures 1 and 2, such as that commercially available from Kayex of Rochester, NY. The furnace was closed and sealed and the furnace control system began the pre-fire vacuum check by closing the inert purge gas inlets and opening the main exhaust valve. The furnace was evacuated and placed under vacuum by pumping the air from within the crystal growth environment. When the pressure was reduced to about 200 mtorr, the main exhaust valve was closed, the purge inlet was opened and the furnace was filled with argon (Ar), to a pressure of about 100 torr. This cycle of reducing the pressure and then back-filling with an inert process gas was repeated two additional times. After the third cycle, the furnace was back-filled to a pressure of about 15 torr and the process gas inlets and main exhaust valves were balanced to provide for a flow rate of about 100 slm (standard liters per minute or liters per minute adjusted for standard temperature and pressure) through the pull chamber, the growth chamber and the exhaust piping. The gaseous environment within the crystal puller was monitored for

about 10 minutes, with samples collected at a rate of one about every minute from Port 1, Port 2 and Port 3. The samples were then passed to a Qualitorr Orion Quadrupole Gas Mass Analyzer System (commercially available from the UTI Division of MKS from Walpole, MA) as the detector.

Monitoring sample results are shown below in Table 1.

Referring to Table 1, samples taken from the crystal growth chamber (Port 1) and the LHS exhaust (Port 3) were well within the acceptable oxygen and nitrogen content ranges for automatic start-up of the furnace heater. However, monitoring results for N₂ and O₂ in the RHS exhaust (Port 2) were out of range for automatic starting. Because experience has shown it to be very unusual for the RHS and LHS exhaust samples to be different by more than about 10%, the crystal puller operator chose to abort the crystal production run and inspect the crystal growth chamber, wherein it was discovered that a plug of silicon oxide was lodged in the RHS Exhaust pipe. The plug was removed and the run restarted without incident.

In this regard it should be noted, with respect to the water content levels, that as explained above these levels may be high in a crystal puller at ambient conditions. As a result, experience with a given puller may lead to the conclusion that levels in excess of 1000 ppmv are acceptable for start-up, because the levels are quickly reduced once the heaters are "fired" (the water quickly being vaporized and swept out of the crystal puller by the process purge gas flow).

Table 1.
Pre-fire monitoring results.

Sample Port	N ₂ (ppmv)	N ₂ UCL	O ₂ (ppmv)	O ₂ UCL	H ₂ O (ppmv)	H ₂ O UCL
Port 1	50	100	14	30	623	200
Port 2	70	50	17	10	1417	200
Port 3	14	50	1	10	1181	200

Without monitoring the pre-fire vacuum check conditions with the method of the present invention, the plugged RHS exhaust pipe would not have been discovered prior to beginning the crystal growth process and the run would have commenced with the extreme likelihood of not producing any useable crystal. The plugged exhaust pipe would have caused the purge gases flowing through the growth chamber to be very unevenly distributed around the crystal. Most of the flow would be going to the left-hand side of the furnace. The usual consequences of such a condition is a build-up of oxide particles above the melt on the right-hand side. As the mass of small particles collects together and grows, larger particles will be created and many will become detached. Occasionally, one of these particles may be swept into the melt by gas currents created by the asymmetric flow of purge gas. A large particle of silicon oxide on the melt surface during crystal growth will generally become attached to the growing crystal and cause the loss of zero dislocation structure.

Additionally, an asymmetric flow of purge gases around the crystal will generally result in an increase in the carbon content of the crystal. This occurs because the asymmetric gas flow creates a lower pressure on the lower flow side of the growth chamber and by aspiration draws gases containing carbon monoxide (CO) from the lower portion of the growth chamber to the melt surface. The CO readily reacts with the liquid silicon and increases the carbon content of the melt.

Example 2

Nineteen single crystal silicon growth runs were completed in accordance with the Czochralski process using a 300 mm crystal growth furnace commercially available from Kayex of Rochester, NY in order to demonstrate the utility and value of an automatic carbon monoxide (CO) monitoring

and alarm system. The monitoring system was as described above and as shown in Figs. 1 and 2 employing a Qualitorr Orion Quadrupole Gas Mass Analyzer System (RGA) (commercially available from the UTI Division of MKS, Walpole, MA). Samples were collected at intervals of one about every five minutes over the length of the main body of the ingots, based on the above described protocols. All of the collected data for each ingot was then averaged, to determine a single data point for each (as shown in Figs. 3 and 4, further discussed below).

At the start of the experiment, the high CO alarm system was not yet automated; thus, the crystal puller operator was required to be vigilant in observing the gas composition displayed on the RGA video monitor. After 11 runs, indicated by runs labeled A through K on Figures 3 and 4, alarm limits (upper control limits or UCL) were set based upon the measured concentrations of CO above and adjacent to the melt at Port 1 (P1) and in the exhaust gases at Port 2 (P2) and Port 3 (P3). The alarm limits, as shown in Figures 3 and 4, were set for each port based upon control charting or statistical process control by setting the UCLs for each port at a value equal to the mean CO concentration observed in the first eleven runs plus three times the standard deviation observed in the same eleven runs.

Figure 4 graphically shows the difference in CO concentrations at P2 and P3 as compared to the CO concentrations at P1. The difference in CO at P2 and P3 is plotted in order to identify a condition of unbalanced purge flow through the crystal growth chamber and in particular around the crystal. After the first eleven runs, UCLs for the difference in CO concentration at P2 and P3 and the CO concentration at P1 were set. The UCLs were again calculated as the mean value of the first eleven runs plus three times the standard deviation associated with the same eleven runs. The results of Figure 4 show that during body growth of the crystal in run M, the difference between the

CO concentration at P2 and P3 exceeds the UCL. Since this was a first time occurrence, no corrective action was prescribed. However, during the runs after M, the difference between P2 and P3 CO concentration continued to increase. Also, starting with run N, the CO in the gas measured above the melt at P1 increased above the UCL. This is a condition that would be expected to cause the silicon melt to increase in carbon composition by reaction of CO in the gases at the melt surface with the molten silicon. To substantiate this, carbon measurements were obtained for the crystal from run O and several crystals from runs with CO below the UCL. As seen in Figure 5, the carbon in crystal from run O was higher than in the other crystals.

The typical silicon crystal has a very shiny (highly reflective) surface when it is removed from the crystal growth furnace. Portions of the crystals produced between runs M and P had a flat (not reflective) gray surface. Photographs of the surface of the crystals from run E (low CO at P1) and run N (high CO at P1) and a microphotograph of the SiC crystallites formed on the surface of a crystal similar to the crystal from run N are given in Figure 6.

The monitoring data from Run N suggested the flow of Argon in the RHS exhaust (P2) was constricted during the run causing an unbalance in the Ar purge around the crystal. The unbalanced purge was diluting the CO in the LHS exhaust stream monitored by P3. As a consequence of the unbalanced purge around the crystal, gases containing a high concentration of CO were being aspirated into the upper portion of the crystal growth furnace from the lower portion of the crystal growth furnace by the increased flow differential between the LHS exhaust pipe and the RHS exhaust pipe. Corrective action consisting of replacing the protective linings in the graphite upper sections of the exhaust pipes was taken before Run Q. As seen in Figs. 3 and 4, the CO concentration at all three sampling ports was

back to normal in Run Q and following. Carbon data available for Run S was found to be typical.

As experience is gained on out of control situations as represented by this example, corrective actions or preventive maintenance schemes can be developed to optimize process performance to improve crystal quality and reduce manufacturing costs.

Example 3

Sixteen crystal growth runs were conducted in accordance with the Czochralski process using a 300 mm crystal growth furnace commercially available from Kayex of Rochester, NY in order to demonstrate the utility and value of an automatic monitoring and alarm system for detecting nitrogen and/or oxygen resulting from, for example, a leak. The monitoring system was as described above and as shown in Figs. 1 and 2 employing a Qualitorr Orion Quadrupole Gas Mass Analyzer System (RGA) (commercially available from the UTI Division of MKS, Walpole, MA). Samples were collected at intervals of one about every five minutes during the growth process, based on the above described protocols. All of the collected data for each ingot was then averaged, to determine a single data point for each (as shown in Figs. 7-10, further discussed below).

In this example, the alarm system was not yet automated; thus, the operator was required to be vigilant in observing the gas composition displayed on the RGA video monitor. After 11 runs, indicated by runs labeled A through K on Figs. 7 through 10, alarm limits (upper control limits or UCL) were set based upon the measured concentrations of nitrogen above and adjacent to the melt at Port 1 (P1) and in the exhaust gases at Port 2 (P2) and Port 3 (P3). The alarm limits, as shown in Figs. 7 through 10, were set for each port based upon control charting or statistical process control by setting the UCLs for each port at a value equal

to the mean nitrogen concentration observed in the first eleven runs plus three times the standard deviation observed in the same eleven runs.

5 The runs were completed without incident until Run L. During Run L, the puller was leak tight at the pre-fire check as indicated at point number 4 in Figs. 7 and 8. However, during the growth of the crystal, the operator noted that a leak was present during the body growth of the crystal. The leak was observed when Port 1 was monitored but not Port 2, as indicated at point number 4 in Figs. 9 and 10. The level of N_2 was well above expectation at Port 1 but not above expectation at Port 2. Port 3 was also monitored but was identical to Port 2. The high concentration of N_2 at Port 1 but not at Port 2 indicated that the leak was near sampling port 1. It was suspected that the leak was in a granular poly feeding mechanism near port 1. An effort was made to stop the leak but was not successful. It was decided to allow the crystal cycle to continue to determine the effect on zero defect growth of a leak of this magnitude. It was quickly decided that zero defect crystal could not be produced due to the leak and the cycle was terminated.

15 In three crystal growth cycles prior to L and one following L, N_2 was noted to be above expectation during the pre-fire check with the RGA (see points 1, 2, 3 and 5 in Figs. 7 and 8). Corrective action was taken before crystal growth, and as a result of the corrective action, no leak was observed during crystal growth as indicated by points 1, 2, 3, and 5 in Figs. 9 and 10.

25 Without monitoring the gases at Port 1 with the RGA, an air leak would not have been identified as the cause of the failed crystal growth cycle. In this case, the information on the leak from the RGA and the failure to grow a zero defect crystal, led to the decision to shorten the cycle and save valuable time which was used to begin the next cycle.

Express Mail Label
No. EL 739386828 US

39

MEMC 00-1100(2808.1)
PATENT

- - - - -

In view of the above, it will be seen that the several objects of the invention are achieved. As various changes could be made in the above material and processes without departing from the scope of the invention, it is intended that all matter contained in the above description be interpreted as illustrative and not in a limiting sense.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400
1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482
1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
1512
1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
1569
1570
1571
1572
1573
1574
1575
1576
1577
1578
1579
1580
1581
1582
1583
1584
1585
1586
1587
1588
1589
1590
1591
1592
1593
1594
1595
1596
1597
1598
1599
1600
1601
1602
1603
1604
1605
1606
1607
1608
1609
1610
1611
1612
1613
1614
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634
1635
1636
1637
1638
1639
1640
1641
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663
1664
1665
1666
1667
1668
1669
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725
1726
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736
1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
1793
1794
1795
1796
1797
1798
1799
1800
1801
1802
1803
1804
1805
1806
1807
1808
1809
1810
1811
1812
1813
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848
1849
1850
1851
1852
1853
1854
1855
1856
1857
1858
1859
1860
1861
1862
1863
1864
1865
1866
1867
1868
1869
1870
1871
1872
1873
1874
1875
1876
1877
1878
1879
1880
1881
1882
1883
1884
1885
1886
1887
1888
1889
1890
1891
1892
1893
1894
1895
1896
1897
1898
1899
1900
1901
1902
1903
1904
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943
1944
1945
1946
1947
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
2027
2028
2029
2030
2031
2032
2033
2034
2035
2036
2037
2038
2039
2040
2041
2042
2043
2044
2045
2046
2047
2048
2049
2050
2051
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
2062
2063
2064
2065
2066
2067
2068
2069
2070
2071
2072
2073
2074
2075
2076
2077
2078
2079
2080
2081
2082
2083
2084
2085
2086
2087
2088
2089
2090
2091
2092
2093
2094
2095
2096
2097
2098
2099
2100
2101
2102
2103
2104
2105
2106
2107
2108
2109
2110
2111
2112
2113
2114
2115
2116
2117
2118
2119
2120
2121
2122
2123
2124
2125
2126
2127
2128
2129
2130
2131
2132
2133
2134
2135
2136
2137
2138
2139
2140
2141
2142
2143
2144
2145
2146
2147
2148
2149
2150
2151
2152
2153
2154
2155
2156
2157
2158
2159
2160
2161
2162
2163
2164
2165
2166
2167
2168
2169
2170
2171
2172
2173
2174
2175
2176
2177
2178
2179
2180
2181
2182
2183
2184
2185
2186
2187
2188
2189
2190
2191
2192
2193
21